Study of Adsorption and Separation Behavior of Rare Earths and Americium with Novel Chelating Adsorbents

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授　与　学　位	博士（工学）
学位授与年月日	平成２３年９月１４日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）量子エネルギー工学専攻
学位論文題目	

Study of Adsorption and Separation Behavior of Rare Earths and Americium with Novel chelating Adsorbents

（新規キレート吸着剤による希土類元素及びアメリシウムの吸着・分離挙動に関する研究）

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論文内容要旨

Nuclear power is believed to play an important role for long-term energy security and global warming prevention in the 21st century. On the other hand, to ensure a sustainable development of nuclear energy in the future, it is necessary to establish a closed nuclear fuel cycle to save uranium resource and minimize radioactive waste accumulation. However the elements which contribute most to the long term radiotoxicity are the minor actinides (MA=Am, Cm, etc.) after a few hundred years. The purpose of this study is to separate MA from main FP in high level liquid waste (HLLW), especially the separation of trivalent MA from the rare earths (RE) is a key step that remains to be solved owing to their chemical similarity. In this study trivalent Am is used as the representative of minor actinides.

For this purpose, two partitioning processes are designed using extraction chromatography: the single column separation process and the two-column separation process. Compared to solvent extraction, extraction chromatography which uses solid state adsorbent has many attractive advantages, such as very limited organic extractant and diluent utilization, compact equipment and less waste accumulation, so that has a great potential in the application for the partitioning of the minor actinides. In extraction chromatography, an inert silica-based macroporous support is impregnated with an organic extractant, to produce a solid adsorbent, capable of selectively removing certain metal ions from the aqueous solution. Therefore extraction chromatography combines the selectivity of the solvent extraction process with the simplicity and multistage character of the column chromatographic system. Three kind of chelating organic extractants *iso*hexyl-BTP (2,6-bis(5,6-bis (4-methylpentyl) -1,2,4-triazin-3-yl)pyridine), *iso*butyl-BTP (2,6-bis(5,6-dibutyl-1,2,4- triazin-3-yl)pyridine) and TODGA (N,N,N',N'-tetraoctyl -3-oxapentane-1,5-diamide) are chosen not only for their good adsorption to Am and RE, but also for the composition of

containing C, H, O and N atoms only.

In the single column separation process, a novel chelating adsorbent *iso*hexyl-BTP was synthesized. The adsorption, desorption and separation behavior of Am and typical FP elements onto this adsorbent in HNO_3 solution were examined by batch and column experiments.

In batch experiments, Am(III) had much stronger adsorption onto *iso*hexyl-BTP adsorbent in 2-3 M HNO_3 solution than RE, especially light RE elements (La-Sm, Y). Distribution ratio of Am was more than 1,000 cm^3/g in 3 M HNO_3 solution after 3 h contact time and Am could be eluted by H_2O from adsorbed *iso*hexyl-BTP adsorbent. For RE elements, adsorption of Dy(III) was dominantly higher than other RE(III), and light RE(III) showed almost no adsorption onto *iso*hexyl-BTP adsorbent under experiment condition. Therefore, adsorption ability of trivalent RE onto *iso*hexyl-BTP adsorbent in 3 M HNO_3 solution was: heavy RE > middle RE > light RE. The adsorption process of Dy(III) onto *iso*hexyl-BTP adsorbent followed Langmuir isotherm adsorption equation and could be expressed by Langmuir monomolecular layer adsorption mode. The maximum adsorption capacity of Dy(III) onto *iso*hexyl-BTP adsorbent was estimated to be 0.14 mmol/g at 298 K. In addition, compared to other tested FP elements, Pd(II) had strongest adsorption onto *iso*hexyl-BTP adsorbent in 0.1 M to 4 M HNO_3 solution and more than 90 % of a adsorbed Pd could be eluted from the adsorbent by 0.01 M thiourea (CH_4N_2S) solution at 323 K.

In stability experiments, *iso*hexyl-BTP adsorbent had relative good stability against 0.1 M, 1 M and 3 M HNO_3 solution after 4 months contact time at room temperature. The values of total organic carbon (TOC) in liquid phase which reflected the leakage amount of *iso*hexyl-BTP from adsorbent were 14 ppm, 24 ppm and 230 ppm in 0.1 M, 1 M and 3 M HNO_3 solution after 4 months, respectively. However, under γ-irradiation, the concentration of total organic carbon in liquid phase increased with the increase of irradiation dose (equal to contact time) and the increase of concentration of HNO_3 solution. The TOC values were 42 ppm, 800 ppm and 6,100 ppm after contact time of 4 months with γ- irradiation in 0.1 M, 1 M and 3 M HNO_3 solution, respectively. Compared to contrast sample, the irradiation dose had evident effect on the leakage amount of *iso*hexyl-BTP from adsorbent at room temperature even in 3 M HNO_3 solution. Thus, radiolytic stability of *iso*hexyl-BTP adsorbent was not sufficient under long time (4 months) γ-irradiation (dose rate 36-41 Gy/h) in 3 M HNO_3 solution at room temperature.

According to the results of partitioning column experiments at 298 K and 323 K, a reasonable single column separation process was designed by temperature control. In this process, Am(III) could be separated successfully from most FP elements by feeding simulated HLLW solution at 298 K, washing no or weak adsorption group elements with 3 M HNO_3 solution at 298 K and eluting Am with H_2O at 323 K. Under these experimental conditions, most of Am could be separated from other elements in HLLW directly. The use of 3 M HNO_3 solution at 298 K for feed and washing were expected a diminution of radiolytic and chemical damage for the absorbent due to elimination of ^{137}Cs and ^{90}Sr at early separation stage. This single

column separation process had high selectivity to Am(III) from HLLW and simple operation, but the stability of *iso*hexyl-BTP adsorbent was not sufficient for long time contact with 3 M HNO_3 solution and irradiation.

In the two-column separation process, two kinds of TODGA and *iso*butyl-BTP chelating adsorbents were synthesized. Adsorption and separation behavior of Am and some typical FP elements onto TODGA adsorbent in HNO_3 solution were examined by batch and column experiments. The adsorption and separation behavior of Am and heavy RE elements onto *iso*butyl-BTP adsorbents in 0.01 M HNO_3 solution were examined by batch and column experiments also.

In batch experiments, Am(III) showed strong adsorption affinity onto TODGA adsorbent in 3 M HNO_3 solution and reached equilibrium state within 0.5 h. Distribution ratio of Am was more than 10000 cm^3/g on equilibrium state and it was difficult to desorb Am from loaded TODGA adsorbent by distilled water. For RE(III) elements, heavy RE (including Y) showed strong adsorption onto TODGA adsorbent in 3 M HNO_3 solution. The adsorption ability of them onto TODGA adsorbent was: heavy RE > middle RE > light RE. In addition, compared to other tested FP elements, Zr(IV) had strongest adsorption onto TODGA adsorbent in 1 M to 5 M HNO_3 solution and more than 91 % of the adsorbed Zr(IV) could be eluted from the adsorption by 0.01 M DTPA (diethylenetriaminepentaacetic acid) solution at 298 K. The adsorption processes of Y(III) and Zr(IV) onto TODGA adsorbent followed Langmuir isotherm adsorption equation and could be expressed by Langmuir monomolecular layer adsorption mode. At the same time, the value of the standard enthalpy change of Y(III) in this adsorption process was determined to be -2.49 $KJ \cdot mol^{-1}$ by the Van't Hoff equation, which indicated that this adsorption process was an exothermic reaction, therefore lower temperature resulted in a stronger adsorption. Compared to RE elements, *iso*butyl-BTP adsorbent had strong adsorption for Am(III) and distribution ratio of Am(III) reached about 200 cm^3/g after 3 h contact time in 0.0001 M HNO_3 solution. *iso*butyl-BTP adsorbent showed no or weak adsorption for light and middle RE in 0.01 M HNO_3.

In stability experiments, the HNO_3 concentration had tiny effect on the leakage amount of TODGA from adsorbent at room temperature. The leakage amounts of TODGA were 24 ppm, 38 ppm and 50 ppm after contact time of 5 months in 0.01 M, 1 M and 3 M HNO_3 solution, respectively. Under γ-irradiation, the leakage amount TODGA increased with the increase of irradiation dose (equal to contact time) and the increase of concentration of HNO_3 solution. The leakage amount of TODGA in liquid phase were 190 ppm, 240 ppm and 400 ppm after 5 months contact time with γ-rays in 0.01 M, 1 M and 3 M HNO_3 solution, respectively. Compared to contrast sample, the irradiation dose had evident effect on the leakage amount of TODGA from adsorbent at room temperature. However, even the TODGA adsorbent contacted with 3 M HNO_3 solution under γ-irradiation about 4 months, the leakage percent of adsorbent was below 4%. This value reflected a small amount of the adsorbent was decomposed by HNO_3 solution and γ-irradiation. Therefore, TODGA adsorbent showed good stability against 3 M HNO_3 and long time irradiation. Similarly to the *iso*butyl-BTP adsorbent, 0.01 M HNO_3 solution had not obvious effect on

the destruction of *iso*butyl-BTP adsorbent under γ-irradiation and less than 1.2 % adsorbent was decomposed after 5 months contact time at room temperature. Thus, *iso*butyl-BTP adsorbent had good stability against 0.01 M HNO_3 and long time irradiation.

In two-column separation process, first column was packed with TODGA adsorbent and the elements in HLLW could be separated to three groups. The second column packed with *iso*butyl-BTP adsorbent for the separation of MA from heavy RE-Zr-Pd. As a conclusion of two column separation method, in the first TODGA column, all of the elements in simulated HLLW were separated into (1) non-adsorption group such as Ru, Rh and a portion of Mo (by 3 M HNO_3 washing solution); (2) Sr, Ce, Nd, and a portion of Mo and Eu, a small portion of Gd (by H_2O elution solution); (3) Y-Zr-Pd-Eu-Gd-Dy-Am group (by 0.01 M DTPA elution solution), respectively, at 323 K. After decomposition of DTPA in (3) group effluent, Am was fed into the second *iso*butyl-BTP column because of their similar adsorption behavior onto TODGA adsorbent. The Am-containing effluent was then applied to the second one and was separated into three group: (1) non-adsorption group such as Y, Zr, Eu, Gd and Dy (by 0.01 M HNO_3 washing solution); (2) ^{241}Am (by H_2O elution solution); (3) Pd was left in adsorbent, respectively, at 323 K. the separation operation of Am from HLLW was successful and the total recovery rate of Am was 85.5%.

Single column separation process can separate Am from most FP elements in HLLW directly by temperature control and recovery yield is 69 % which can be improved using enough washing solution or using organic complex agent as elution solution. The K_d value of Am onto *iso*hexyl-BTP adsorbent is more than 1,000 cm^3/g and separation factor (SF) of Am/RE is more than 100. The adsorption and desorption need relative long time to reach equilibrium state due to relatively slow adsorption kinetics of *iso*hexyl-BTP adsorbent. However, *iso*hexyl-BTP adsorbent has relatively good chemical stability against HNO_3, but radiolytic stability is not sufficient for 4 months irradiation in 3 M HNO_3 solution. On the other hand, the operating procedure of this process is simple.

Two-column separation process can separate Am from most FP elements in HLLW also and recovery yield is 86 % after through two separation columns. The K_d values of Am onto TODGA and *iso*butyl-BTP adsorbents are more than 10,000 cm^3/g and 100 cm^3/g, respectively. The SF value of Am/RE with *iso*butyl-BTP adsorbent is more than 100. The adsorption and desorption reaction can reach equilibrium state in short time due to quick adsorption kinetics of both TODGA and *iso*butyl-BTP adsorbents. In addition, TODGA and *iso*butyl-BTP adsorbent has good stability against γ-ray irradiation in 3 M and 0.01 M HNO_3 solution after 4 months contact time at room temperature, respectively. Compared to single column separation process, recovery yield of Am in two column separation process is high and stability is good, but the operating procedure of this process is relatively complicated.

論文審査結果の要旨

使用済核燃料にはUやPuの他に、Np、Am、Cmといった長寿命マイナーアクチニド(MA)及び様々な核分裂生成元素(FP)が含まれている。現行のPUREX再処理プロセスでは、Npの一部とAm, Cmのほぼ全量が回収できず、FPとともに高レベル廃液(HLLW)中に導かれている。HLLWはガラス固化体として地層処分される計画であるが、MA等の長寿命核種による環境への長期的な放射能リスクが懸念されている。MAをHLLWから分離除去して将来高速炉や加速器駆動システム（ADS）による核変換処理を行うことは、先進的な核燃料サイクル体系を構築していく上で極めて重要な課題となっている。一方、HLLWから三価MA（AmとCm）の分離、特に類似な化学性質を有する三価希土類（RE）との相互分離が大変困難である。これまでに種々の抽出剤を用いる溶媒抽出法を中心に多くの分離方法が研究されてきたが、実用化に繋がる効率的な分離技術は未だ開発されていない。本研究は、抽出剤を多孔性担体に含浸担持させた吸着剤を用いる抽出クロマトグラフィー法に着目し、溶媒抽出法に比べて分離効率が高く、且つ廃棄物量の顕著な低減化が期待できる革新的な三価希土類・MA分離プロセスの開発を目指している。

本論文は新規キレート吸着剤による希土類元素及びアメリシウムの吸着・分離挙動の研究に関するもので、全5章からなる。

1章は序論であり、本研究の背景と目的を述べている。

2章は実験方法を記述し、シリカ担持型キレート吸着剤の合成方法、種々の金属イオンの定量分析法、吸着剤による金属イオンの吸着性能及び脱着性の評価試験、カラム分離試験、ならびに吸着剤の化学的安定性（耐硝酸性、耐放射線性）評価実験の方法を述べてある。

3章では窒素原子を配位子とする新規isohexyl-BTP吸着剤によるAmとRE等のFP元素の吸着および分離挙動を実験的に調べ、また吸着剤の耐硝酸性および耐γ線性を評価している。2～3M硝酸溶液においてAmがRE元素（特にLa-Sm, Y）に比べ遥かに高い吸着性を示し、吸着したAmを水で脱着できる可能性を見出している。特異的な吸着性を示すPdに対してはチオ尿素錯化剤による効果的な脱着方法を見出し、Amとの分離可能性を指摘している。Amと類似な吸着挙動を示すDyの吸着機構や吸着量を詳細に評価している。また、カラム実験では吸着と脱着の温度を制御することによって、模擬HLLWから良好なAm分離効果が得られている。一方、isohexyl-BTP吸着剤は低濃度硝酸中で比較的良好な耐γ線性を示しているが、1M以上の高濃度硝酸溶液中では長期間のγ線照射による性能劣化が顕著に現れた。本研究の結果に基づいて単一カラムによるMA直接分離プロセスを提案し、今後吸着剤の安定性が十分改善されれば、HLLWからのMA分離システムの大幅な簡素化が期待される。

4章では酸素原子を配位子とするTOTGA吸着剤及び窒素原子を配位子とするisobutyl-BTP吸着剤による2カラムMA分離プロセスを提案している。1段目のTOTGA吸着剤は3M硝酸溶液においてAmに強い吸着性を示し、吸着したAmを錯化剤DTPAで脱着できることを見出している。模擬HLLWのカラム分離試験ではAmは重RE及びZrとともに回収し、他のFPから良好に分離できることを確認している。更に、2段目のisobutyl-BTP吸着剤は希硝酸(0.01M)中で高いAmとREの高い分離性能を有することを確認している。TOTGA吸着剤は高濃度硝酸中で長時間γ線照射後も優れた安定性を示し、isobutyl-BTP吸着剤は希硝酸中で良好な耐γ線性を示している。吸着剤の分離性能及び安定性評価結果により、提案した分離プロセスはHLLWからのMA分離に応用可能な重要な成果である。

5章はまとめであり，本研究の成果を総括している。

以上，要するに本論文は新規キレート吸着剤による高レベル廃液からの三価希土類・MA高度分離に関する研究をまとめたもので量子エネルギー工学に貢献するところは少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。